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Sunset Reservoir Wells Perchlorate Investigation

Presented by
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Presented to
United States Environmental Protection Agency

April 12, 2013

Stable Isotope Analysis ClO_4 - 1

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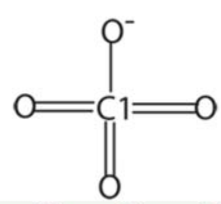
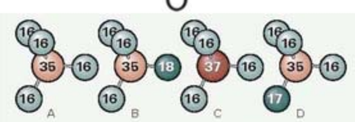
- $^{16}O = 16$
- $^{17}O = 17$
- $^{18}O = 18$
- $^{35}Cl = 35$
- $^{37}Cl = 37$
- $^{35}Cl^{16}O_4 = 99$
- $^{37}Cl^{16}O_4 = 101$
- $^{37}Cl\,^{17}O_4 = 105$
- $^{35}Cl\,^{18}O_4 = 107$
- $^{37}Cl^{18}O_4 = 109$





Perchlorate isotopomers: The perchlorate molecule (A) usually incorporates the most abundant stable isotopes of chlorine and oxygen, ^{16}O and ^{35}Cl. A small percentage will include one or more ^{18}O isotopes (B), some will have ^{37}Cl instead of ^{35}Cl (C), and perchlorate of atmospheric origin is more likely to incorporate the rare ^{17}O atom (D).

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Stable Isotope Analysis ClO_4- 2

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1. The Oceans of the Earth have a ratio of ^{16}O to ^{18}O of 49,000:1
2. This is based upon Vienna Standard Mean Ocean Water (VSMOW)
3. Deviation from this mean is calculated by $\delta^{18}O = (^{18}O/^{16}O)sample / (^{18}O/^{16}O)vsmow - 1 = \delta^{18}O = 0.0‰$

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Stable Isotope Analysis ClO_4- 3

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1. The Oceans of the Earth have a ratio of ^{16}O to ^{17}O of 263,000:1
2. This is based upon Vienna Standard Mean Ocean Water (VSMOW)
3. Deviation from this mean is calculated by $\Delta^{17}O = (1 + \delta^{17}O)/(1 + \delta^{18}O)0.525$ vsmow $= \Delta^{17}O = 0.0‰$

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Stable Isotope Analysis ClO_4- 4

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1. Oceans of the Earth have a ratio of ^{35}Cl to ^{37}Cl of 76:24
2. This is based upon the Standard Mean Ocean Chloride (SMOC).
3. Deviation from this mean is calculated by $\delta^{37}Cl = (^{37}Cl/^{35}Cl)$ sample / $(^{37}Cl/^{35}Cl)$smoc – 1 Ocean Water $\delta^{37}Cl = 0.0‰$

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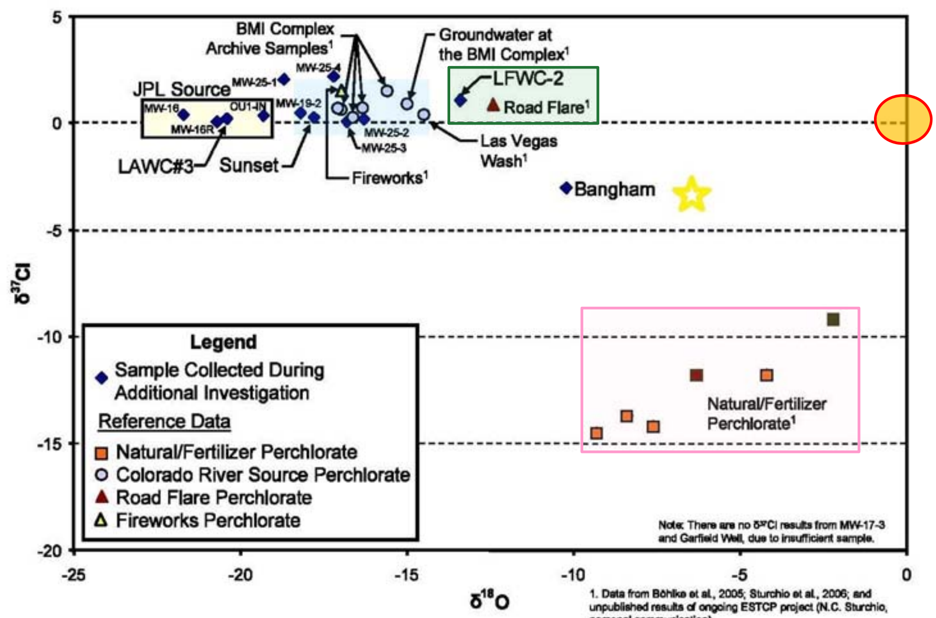
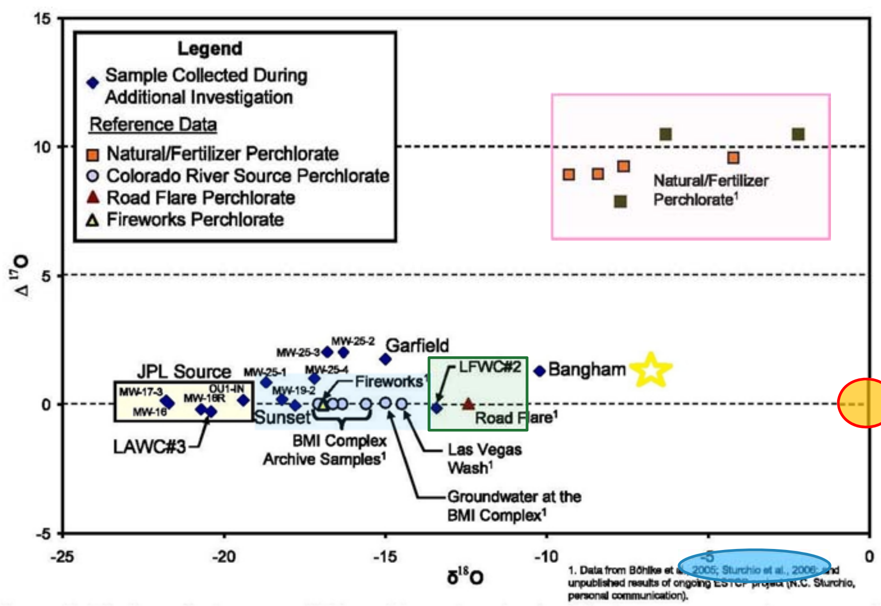
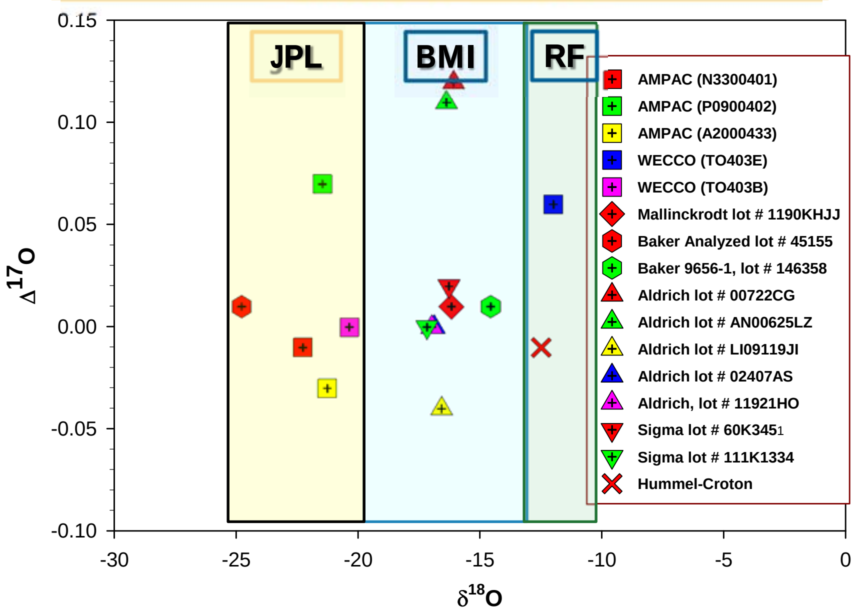
SIA of ClO_4 $\delta^{37}Cl$ vs. $\delta^{18}O$ in the Raymond Basin



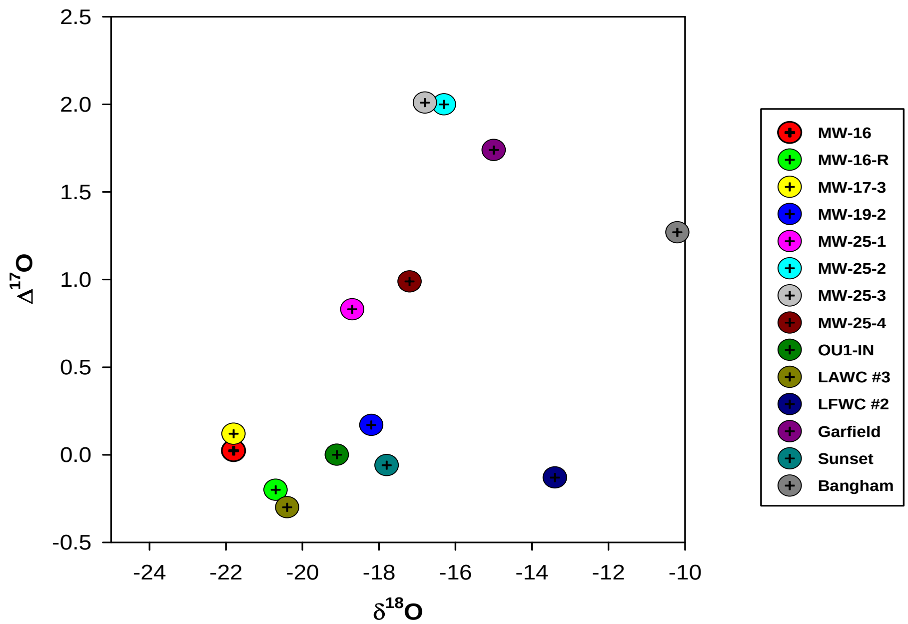
SIA of ClO_4 $\Delta^{17}O$ vs. $\delta^{18}O$ in the Raymond Basin



Industrial Samples SIA of ClO_4 $\Delta^{17}O$ vs. $\delta^{18}O$ Sturchio et al. 2006



Well Samples SIA of ClO_4 $\Delta^{17}O$ vs. $\delta^{18}O$



Biodegradation of ClO_4 $\delta^{37}Cl$ vs. $\delta^{18}O$ by SIA

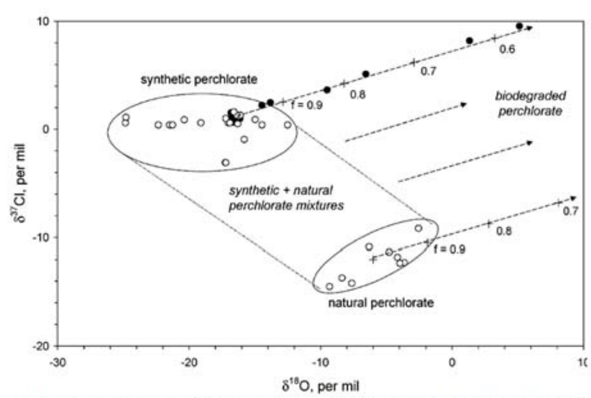
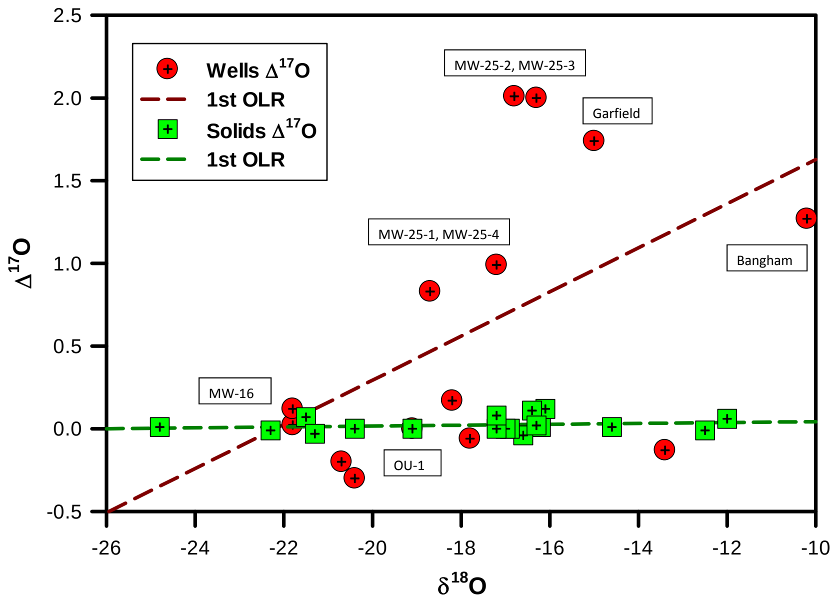


FIGURE 4. Schematic relation between characteristic $\delta^{18}O$ and $\delta^{37}Cl$ values (per mil) of synthetic and natural perchlorate samples (open circles are data from refs *2* and *22*); expected isotopic compositions of mixtures of synthetic and natural perchlorate; and the isotopic compositions of residual perchlorate during biodegradation (where extent of biodegradation is given by *f*, the residual fraction, for representative epsilon values of $\epsilon^{18}O = -36.3‰$ and $\epsilon^{37}Cl = -14.5‰$). Filled circles are data from the present study, which was conducted using synthetic perchlorate.

Biodegradation Impact on ClO_4 in the Raymond Basin



Road Flares

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1. Why would LFWC #2 be influenced by road flares?
2. How many tons of road flare perchlorate would have had to have been released to have produced 4 ppb?
3. Where would road flare perchlorate be disposed to influence only this one well?
5. Most perchlorate in road flares is consumed during combustion
6. Is there any evidence for an unusual number of road flares used in northern Altadena between 1985 and 2005?
7. Notably, there is only one datum for "Road Flares" and only one datum for "LFWC Well #2".
8. These two points do not actually match
9. There are other industrial sample with similar values that are not from "Road Flares" (Baker 9656-1 and WECCO)

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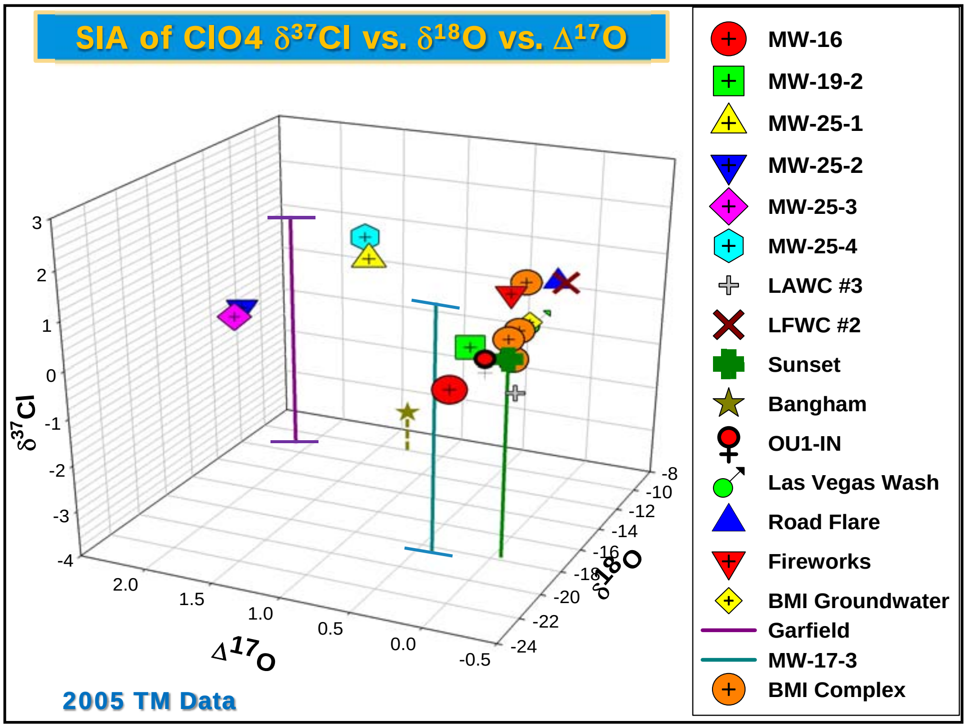
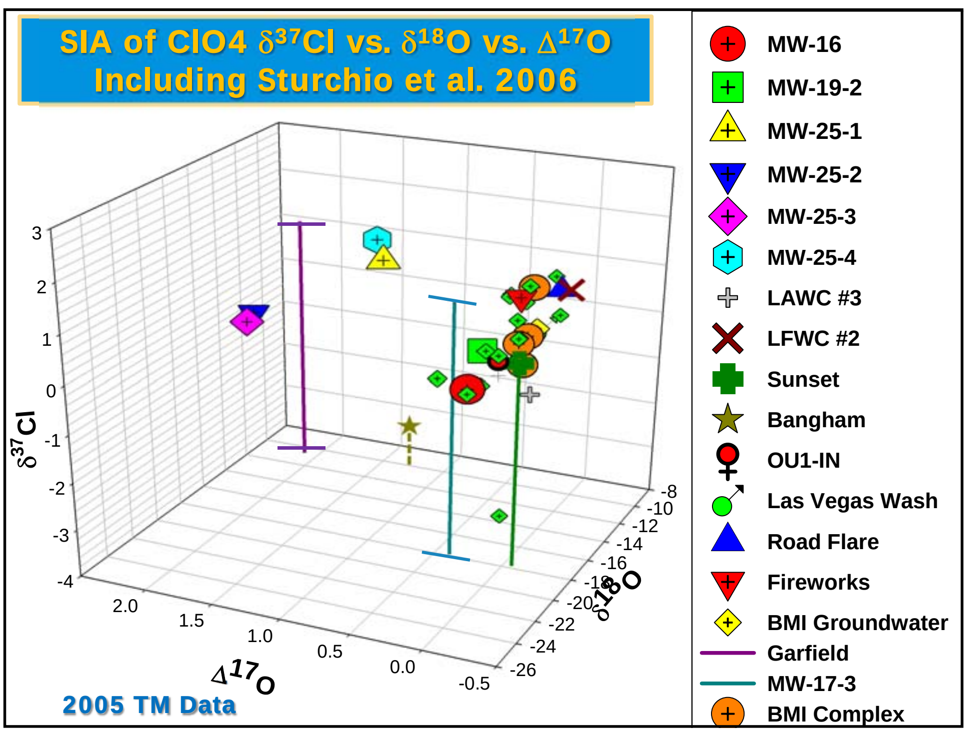


SIA of ClO4 δ37Cl vs. δ18O vs. Δ17O
δ37Cl
3
2
1
0
-1
-2
-3
-4
Δ17O
2.0
1.5
1.0
0.5
0.0
-0.5
δ18O
-8
-10
-12
-14
-16
-18
-20
-22
-24
2005 TM Data
MW-16
MW-19-2
MW-25-1
MW-25-2
MW-25-3
MW-25-4
LAWC #3
LFWC #2
Sunset
Bangham
OU1-IN
Las Vegas Wash
Road Flare
Fireworks
BMI Groundwater
Garfield
MW-17-3
BMI Complex



SIA of ClO4 δ37Cl vs. δ18O vs. Δ17O
Including Sturchio et al. 2006
δ37Cl
3
2
1
0
-1
-2
-3
-4
Δ17O
2.0
1.5
1.0
0.5
0.0
-0.5
δ18O
-8
-10
-12
-14
-16
-18
-20
-22
-24
-26
2005 TM Data
MW-16
MW-19-2
MW-25-1
MW-25-2
MW-25-3
MW-25-4
LAWC #3
LFWC #2
Sunset
Bangham
OU1-IN
Las Vegas Wash
Road Flare
Fireworks
BMI Groundwater
Garfield
MW-17-3
BMI Complex

Stable Isotope Analysis of Nitrate

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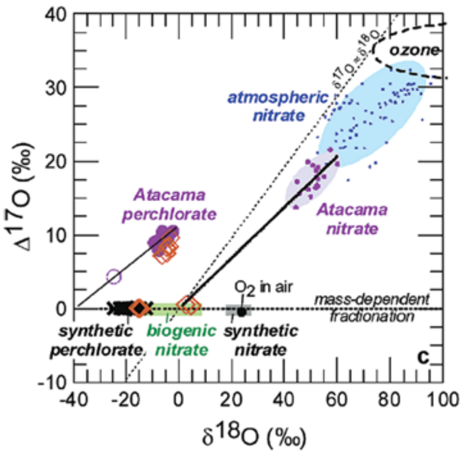

"PerchlorateIsotopeForensics", Bölke, Sturchio, Gu, Horita, Brown, Jackson, Balista, Hatzinger, Anal Chem. 2006,44,7838–7842

"The association between nitrate and perchlorate is potentially important because (1) both compounds are produced in the atmosphere, and both are abundant in the Atacama Desert salt deposits and derivative fertilizers; (2) both compounds are susceptible to microbial reduction in anaerobic conditions but tend to be persistent in aerobic conditions; and (3) groundwaters with elevated perchlorate concentrations commonly also contain nitrate..."

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Stable Isotope Analysis of Nitrate

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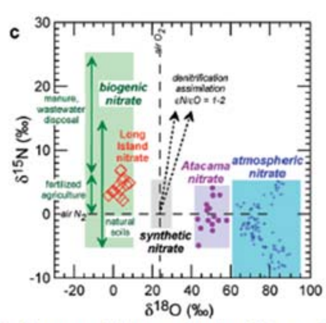

FIGURE 2. Summary of isotope data for ClO_4^- and NO_3^- in groundwater samples (Table 1 and Table S1 in the Supporting

"Atacama Perchlorate as an Agricultural Contaminant in Groundwater: Isotopic and Chronologic Evidence from Long Island, NewYork", Bölke, Hatzinger, Sturchio, Gu, Abbene, Mroczkowski, Environ.Sci.Technol.2009,43,5619–5626

"Isotopic analyses of the Death Valley NO_3^- deposits indicate a large fraction of the NO_3^- may be atmospheric in origin, whereas the remainder is presumed to have formed via microbial nitrification. Similar processes were hypothesized to account for NO_3^- in the Atacama NO_3^- deposits based on isotopic analyses with a larger fraction due to Atmospheric origin."

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Stable Isotope Analysis of Nitrate

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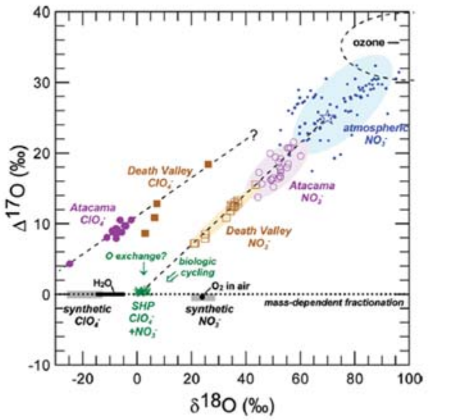

FIGURE 3. Relations between $\Delta^{17}O$ and $\delta^{18}O$ in ClO_4^- and NO_3^-

"Isotopic Composition and Origin of Indigenous Natural Perchlorate and Co-Occurring Nitrate in the Southwestern United States", Jackson, Bölke, Gu, Hatzinger, Sturchio, Environ.Sci.Technol.2010,44,4869–4876

"Isotopic analyses of the Death Valley NO_3^- deposits indicate a large fraction of the NO_3^- may be atmospheric in origin, whereas the remainder is presumed to have formed via microbial nitrification. Similar processes were hypothesized to account for NO_3^- in the Atacama NO_3^- deposits based on isotopic analyses with a larger fraction due to Atmospheric origin."

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SIA of Perchlorate

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1. There is no Chilean Nitrate Fertilizer
2. There are no Road Flare influences
3. The "JPL Source" and the BMI Complex are the Same
4. It is not possible to identify different industrial sources by $\delta^{18}O$ analysis
5. Biodegradation is clearly changing the SIA of perchlorate in the Raymond Basin
6. There is only one source of Perchlorate, WECCO

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Conclusions

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- There is Only One Source of Perchlorate
- There are Three Water Courses
- The Water in the Sunset Reservoir Wells is a Blend of these Three
- The Vast Majority of the Perchlorate Found in the Sunset Reservoir Wells Comes from JPL

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